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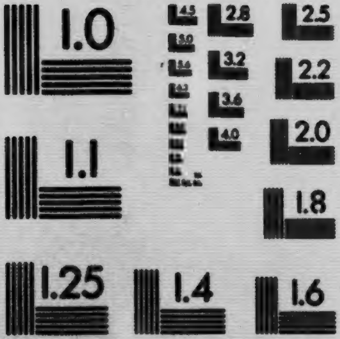

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No. 18.—The Identification of Basic Salts.

BY

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NOTE ON THE
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By W. LASH MILLER and FRANK B. KENRICK

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VI.—*Note on the Identification of Basic Salts.*

By W. LASH MILLER and FRANK B. KENRICK.

(Read May 22, 1901.)

Basic Salts are prepared by the action of water or of bases—potash, ammonia, etc.—on the "normal" salts of most of the metals; in composition they stand intermediate between the normal salts and the oxides (bases), hence the name "Basic Salt." Some are well defined crystalline compounds, but the greater number are known only as amorphous, muddy precipitates, whose composition varies with the concentration and temperature of the solutions and even with the order of mixing the ingredients from which they are prepared.

When the basic salt, besides being amorphous, is insoluble, nonvolatile, and infusible—and this is the rule rather than the exception—it is quite impossible to purify it by any of the usual means; and as the removal of the mother-liquors by washing with water can be resorted to only when special experiments have shown that the composition of the precipitate is not affected by such treatment, even the ultimate analysis of the crude precipitate is not unattended with difficulties.

In the article "Antimoine" in the *Encyclopédie Chimique*, M. Guntz quotes analyses of an oxychloride of antimony by four different chemists; the percentage of chlorine varies from 11·25% to 7·8%. As experiments carried out by Mr. Good (referred to below) show that the substances analysed with such descrepant results were in all probability one and the same chemical compound, M. Guntz's conjecture that the material for analysis was washed too much by some of the analysts, and too little by others, may be accepted as correct.

In such cases the allocation of formulæ is apt to be somewhat [illegible]. Some authors distribute them with a lavish hand, and appear [illegible] in endowing "amorphous finely-divided precipitates" with the [illegible] of chemical individuality; while the more conservative are content to describe the same precipitates as "impure modifications of "compounds" which have already found their way into the text-books. Gladstone took a cautious course; after analysing the precipitate sometimes produced when cupric chloride is dissolved in water, he says:—"Though the salt is evidently somewhat irregular in composition, it approaches nearer [within 2-3%] to the oxychloride

$CuCl_2.2CuO$ than to any other of the eight or nine that have been described by previous investigators."

In the absence of any clearly defined principle of selection much must of necessity be left to individual taste, and as there is wide room for difference of opinion, flat contradictions are not uncommon in the literature of the subject. In Dammer's "*Handbuch der anorganischen Chemie,*" for instance, after detailed descriptions of seven compounds of lead chloride with ammonium chloride, comes the announcement that "according to Randall, none of André's compounds exist"; while with reference to Cross and Suguira's basic oxychlorides of lead, $Pb_{12}Cl_{21}O_4$, $Pb_8Cl_{16}O$, and Pb_4Cl_7O, the editor himself ventures on the criticism, "These were obviously impure, and probably badly analysed." But neither André nor Randall, Cross nor Dammer adduces conclusive evidence in support of his contentions. Mere complexity in the formula is in itself no bar to the genuineness of a chemical compound —Mr Allan's experiments, referred to below, establish beyond question the existence of a basic nitrate of bismuth with the formula $Bi_6H_{26}N_5$[illegible].

Even in the case of so important an article of commerce as white lead, it is still wholly uncertain whether the different varieties are to be regarded as distinct chemical species, as mixtures of a few individuals, or as more or less saturated (solid) solutions of carbon dioxide in lead oxide or in some basic carbonate. It is consequently hardly surprising that success in the manufacture of such substances is conditioned by strict adherence to empirical recipes, any deviation from which may seriously affect the properties—and the value—of the product.

Application of the Phase Rule.

Difficult though it might appear to find any rational basis of classification for these precipitates, there is one large group—viz., all cases where equilibrium is attained between precipitate and mother-liquor—for which the problem is completely solved by two theorems due to Professor Willard Gibbs, which form part of what is commonly known as his "Phase Rule."

These theorems may be stated as follows:—Assuming that the system has arrived at *equilibrium*, at "arbitrary" temperature and pressure, (i) The system can in general consist of no more phases than it has components, (ii) A solution can form one of a group of *n* phases (*n* is the number of the components) only if it has attained a certain composition dependent on the temperature and pressure, and on the chemical and physical nature of the other phases present.

The first theorem does not exclude the possibility of the coexistence of $n+1$ or even $n+2$ phases under certain conditions of temperature and pressure; but if the experiments be carried out at atmospheric pressure in a thermostat set for some temperature below the boiling-point of the solution, the chance of meeting with such special conditions is negligible.

These theorems, which were reached by Gibbs in 1876, in the course of an abstract thermodynamical study of the conditions of equilibrium in heterogeneous systems, have often been verified; their importance, however, as furnishing a means—often the only means—of discovering the chemical individuals in ill-defined muddy precipitates, is only now beginning to be generally realized.

Applied to a particular case, for instance the formation of basic salts by the action of water on the chloride of antimony or on the nitrate of bismuth (temperature and pressure fixed as above), the theorems affirm:

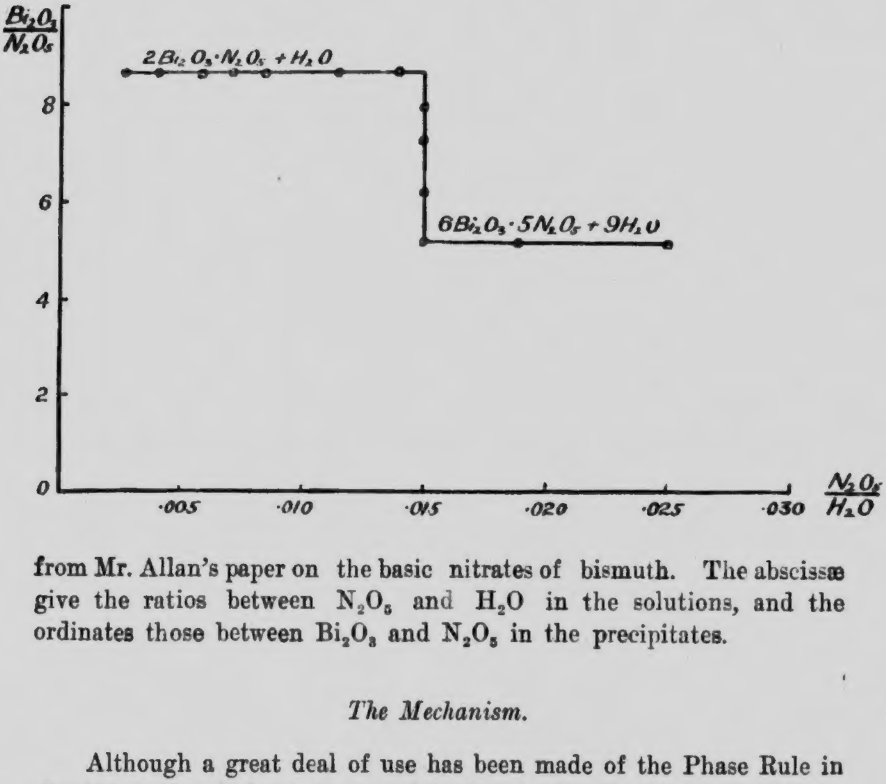
(i) That if the system, which consists of three components (see below), has arrived at equilibrium, not more than three phases can coexist. Of these the solution forms one, the precipitate consequently must be either *one* single homogeneous substance (one phase), or a mixture of *two* phases—for instance, of two basic salts, or of one basic salt with the oxide.

(ii) That if the observed difference in composition between two precipitates, formed by the action of different quantities of water on the same salt, is due to their being mixtures of the same pair of basic salts in different proportions, the composition of the mother-liquors will be the same in the two cases.

The possible cases are thus divided into three groups:—

1. The solutions are identical in composition in different experiments, while the composition of the precipitate varies.—The precipitate is a mixture of two phases.
2. The solutions differ in composition, but the precipitates have the same composition.—The precipitate is a single chemical compound.
3. Both solutions and precipitates vary.—The precipitate is a single phase of variable composition, a "solid solution."

If it were possible to represent the compositions of the solutions by abscissæ, and those of the precipitates by ordinates, the results of a series of experiments could be represented by a curve; perpendicular lines would then correspond to case 1 above, horizontal lines to case 2, and slanting lines to case 3. In a three-component system this is in general not possible. In many cases, however, a pair or pairs of components may be found whose ratio in the solution, or precipitate, changes whenever the composition of the solution, or precipitate, changes, and only then; and since for the interpretation of the results it is only necessary to know whether the composition of solutions and precipitates remains constant or changes from experiment to experiment, it is sufficient to plot these ratios instead of the compositions themselves. An illustration is afforded by the following curve taken from Mr. Allan's paper on the basic nitrates of bismuth. The abscissæ give the ratios between N_2O_5 and H_2O in the solutions, and the ordinates those between Bi_2O_3 and N_2O_5 in the precipitates.



The Mechanism.

Although a great deal of use has been made of the Phase Rule in classifying chemical reactions, and in the study of solutions and alloys, and more recently of such compounds as steel and the various commercial varieties of iron, comparatively little attention has been paid to the mechanism by means of which the results foretold by it are arrived at in the system. The subject is not only interesting in itself, but leads to an extension of the method of identifying chemical individuals among the basic salts, to the case where the precipitation is carried out by means of potash, ammonia, etc., although here the system no longer consists of three components only, and consequently the direct application of the Phase Rule in the manner just illustrated is not possible.

The precipitates produced by the action of water on the nitrate of Bismuth are all of the general formula Bi_2O_3, mN_2O_5, nH_2O; the composition of the solutions also may be expressed in terms of the same substances, Bi_2O_3, N_2O_5, and H_2O, which are henceforward termed the "components" of the System. The compositions of the precipitates and solutions might be expressed in terms of other groups of three,—elements, compounds, or mixtures—but three at least are necessary, and more than three are superfluous; if for example the elements Bi, N, H, and O, be selected, and the quantities of three of them in the solution be known, that of the fourth can be calculated from the stöchiometric relations.

The condition *sine qua non* for the application of the Phase Rule is that equilibrium be reached with respect to all reactions that occur in the system. There is only one sure sign of the attainment of equilibrium, namely, that the compositions of precipitates and solution are found to be independent of the order in which the components were mixed,—the composition of the precipitate must be the same whether $Bi(NO_3)_3$ be mixed with water, or Bi_2O_3 with dilute nitric acid, provided only that the same quantities of the three components be employed in each case. In other words, the quantities of the three components (together with the temperature and the pressure) are sufficient to define the state of the system.

Now, it can be shown by a simple algebraical argument[1] that if A, B, C, and D, be any four phases whatever, formed from the same three components, it is possible either

(i) to mix three of these, e.g., A, B, and C, in such proportions that the components are present in the mixture in the same proportions as they are in D, or

(ii) to prepare a mixture of A and B, and another of C and D in such proportions that the quantities of the three components are the same in both mixtures.

In other words, it is possible with these four phases to build up two systems identical with respect to the amounts of each of the three components, but differing in the nature and composition of the phases composing them, and the condition that the state of the system should be completely defined by the amounts of the components (and temperature and pressure) can be fulfilled only if one of these alternative systems changes spontaneously into the other ; that is, if reactions between the phases

$$A+B+C=D \qquad\qquad A+B=C+D$$

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[1] Van der Waals, quoted by Roozeboom, Rec. Trav. Chim. Pays-Bas 6 265. (1887.)

take place whenever possible, and proceed until one at least of the reacting phases totally disappears. Which of the four will be the first to disappear, depends obviously on the direction of the reaction and on the relative amounts of the different phases present. When the number of phases has been reduced to three, the possibility of a reaction of this nature has vanished.

The occurrence of reactions of this type, then, is the mechanism by means of which the number of phases in a three-component system is kept down to three. If it fails, the state of the system is no longer defined solely by temperature, pressure, and the masses of the components. Experimental evidence of such definition, must therefore be regarded as proof that not more than three phases are present in the (three-component) system.

The result predicted by the second theorem is effected by means of reactions of a second type, which can take place in a three-component system of three phases only if one of the three is capable of continuous variation in composition (a solution).

By dissolving more or less of the solid phases in the solution, it would be possible to construct a whole series of systems—formed of the same amounts of the same components—but differing in the composition of the solutions and in the relative quantities of the solid phases. If only one of these is found to exist in fact, the disappearance of the others must be ascribed to the occurrence of reactions of this second type, which fix the composition of the solution irrespective of the relative quantities of the three phases of which the system is composed.

Extension of the Method.

The two theorems which serve to interpret the experimental results, distinguishing between mixtures and single substances, and identifying the chemical individuals in the precipitates, are thus dependent on the occurrence of reactions of two types:—the first (which does not involve change of composition of any of the phases) resulting in the disappearance of all phases in excess of three; the second (which involves change of composition of the solution) keeping the composition of the solution constant so long as it is in contact with the same pair of basic salts.

The possibility of applying the same method to the study of precipitates formed by potash in solutions of metallic salts, depends on the discovery of conditions under which a fourth component may be added to the system without interfering with the occurrence of these two classes of reactions.

These conditions are:—(*a*) The quantity of water must be large in comparison with that of the second and of the third component; (*b*) The fourth component must remain in the solution and not enter into the composition of the precipitate; (*c*) In each member of a series of experiments there must be a constant ratio between the amounts of the fourth component and of the water in the system.

If the water is present in large excess, (condition *a*) the mass of the solution will be much greater than that of the precipitate, and no reaction occurring in the system can have more than a very slight effect on the total mass of the water contained in the solution. In reactions of the first type (during which the composition of the solution remains unaltered), the quantities of the other components entering or leaving the solution must be still smaller than that of the water; so that reactions of this type leave the total mass of the solution (practically) unaltered.

If now a fourth component be added, the total amount of which in the solution is unaffected by the reaction (condition *b*), this slight variation in the quantities of the other components in the solution will cause such a very slight change in the composition of the latter that the effect of the change in checking the progress of the reaction may safely be neglected; so that the presence of the fourth component, under these conditions, will not interfere with the efficiency of reactions of the first type in keeping down the number of phases to three.

Reactions of the second type (involving changes in the composition of the solution) are of course just as possible when the solution contains a fourth component as when it does not. In order, however, that the solutions over a given pair of basic salts should reach exactly the same composition in different experiments, it is obviously necessary that the concentration of the fourth component in the solution should be the same from case to case. This is provided for by condition *c*. In experiments on the action of caustic potash on solutions of bichloride of copper, for example, H_2O, CuO, and $CuCl_2$ may be selected as components, with KCl as the "fourth component" of the preceding paragraphs; and condition *c* requires that if the quantity of potash added to a given volume of the copper solution should vary from case to case, enough KCl must be added to keep the total amount of potassium per cubic centimetre of water the same in each experiment.

Experiments.

In the spring and summer of 1899 the writers carried out a lengthy series of experiments on the action of potash and ammonia on the chloride of lead. The less basic of the oxychlorides are formed with remarkable slowness; the reaction between N/3 ammonia and lead chloride not coming to a standstill in ten days shaking at 100°*C.* $PbCl_2 3PbO$, however, was formed in a few hours in the cold.

In the winter of 1900-1901, Mr. Good took up the study of the action of water on antimony tri-chloride, presenting his results as a thesis in competition for the 1851 Exhibition scholarship. His observations may be regarded as confirming the individuality of the oxychloride $2SbCl_3 5Sb_2O_3$ in the powder of Algaroth; although in this case also equilibrium is often not attained until days after the precipitation.

Mr. F. B. Allan, Lecturer on Chemistry in the University of Toronto, has just completed a series of experiments on the action of water on the nitrate of bismuth,[1] which he has presented as a thesis for the degree of Ph.D. His results, some of which are represented in the curve on page 38, establish the existence of basic nitrates of the formulæ $Bi_2O_3.N_2O_5.2H_2O$, $2Bi_2O_3.N_2O_5.H_2O$, $6Bi_2O_3.5N_2O_5.9H_2O$; while although precipitates were obtained intermediate in composition between the two last named, they were obviously mixtures. Two of these latter have found their way into the literature as "compounds" $5Bi_2O_3.4N_2O_5.9H_2O$, and $11Bi_2O_3.9N_2O_5.21H_2O$.

Mr. Wilson has been engaged during the past Easter term with experiments on the precipitation of cupric chloride by potash. With N/5 solutions at 85°*C.* the precipitate consists altogether of $CuCl_2.3CuO.2H_2O$ until all the copper is removed from the solution; on further addition of potash the precipitate turns black, no potash remaining in the solution until the precipitate is totally converted into the oxide.

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[1] Amer. Chem. Jour. **25** 307. (1901.)